

## CONDUCTIVITY OF ZIRCONIUM OXIDE ALLOYED WITH LITHIUM OXIDE

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The solid-phase method is used to synthesize polycrystalline samples of zirconium dioxide stabilized with 10%  $Y_2O_3$  (or content) and up to 3%  $Li_2O$ . It is found that the conductivity of the samples increases substantially when  $Li_2O$  is added and reaches its maximum value at 1.7%  $Li_2O$ . The conduction activation energy decreases from 0.85 eV in samples with no  $Li_2O$  added to 0.56 eV in samples containing 1.7%  $Li_2O$ . It is suggested that lithium ions in the  $ZrO_2$  cubic lattice form two types of defects: substitution effects —  $Li_{Zr}^{3-}$  and interstitial defects —  $Li_i^+$ . The latter greatly increase the electrical conductivity of the samples.

Zirconium dioxide based ceramic is an important technological material which has diverse applications because of its unique properties — high strength, hardness, heat resistance, and resistance to corrosive media. There are three polymorphous modifications of  $Zr_2O$ : monoclinic, tetragonal, and cubic. The latter two are high-temperature modifications, but they can be stabilized at lower temperatures by introducing oxides di- and trivalent metals  $CaO$ ,  $MgO$ ,  $Y_2O_3$ , and others. When heterovalent stabilizing additives are added to the structure of zirconium dioxide, oxygen vacancies form and zirconium dioxide possesses ionic conductivity at high temperatures. Articles based on this material sinter practically to zero porosity, which determines their gas density.

The two most important properties listed above promote wide industrial application of ceramics based on stabilized zirconium dioxide in industry. It is sufficient to note that stabilized zirconium dioxide sensors are produced in all industrially developed countries for determining the degree of oxidation of steels and martensite and converter processes as well as the content of oxygen in exhaust gases of diverse metallurgical and power units.

On this basis, investigations of the effect of different impurities, whose introduction at elevated temperatures into the lattice of zirconium dioxide is not precluded, on the electrical and ceramic properties of the articles produced are topical. Contact with lithium-containing materials is possible in the commercial operation of zirconium dioxide articles, and consequently it is important to know how the properties will be changed by the possible interactions. Analysis of published

data [1–3] has shown that for all practical purposes the phase ratios in the system  $Li_2O$ – $Zr(Y)O_2$  have not been studied. It is our view that this is a substantial lacuna in the existing knowledge of the characteristics of zirconium dioxide based ceramics that needs to be filled.

The objective of our work is to study the character of the interaction of small additions of lithium oxide ( $\leq 3\%$ <sup>2</sup>) with cubic  $ZrO_2$  stabilized by 10%  $Y_2O_3$  and the effect of these additives on its electrical properties.

Polycrystalline samples of  $ZrO_2$  with 0.5, 1.0, 1.2, 1.5, 1.7, 1.8, 1.9, 2.0, and 3.1%  $Li_2O$  were obtained by a solid-phase sintering. Lithium carbonate  $Li_2CO_3$  and pre-prepared cubic  $ZrO_2$  stabilized by 10%  $Y_2O_3$  (10YSZ) served as the initial materials for synthesis. Lithium carbonate was first dried in air at 350°C for 4 h. The 10YSZ powder was calcined at 600°C for 4 h in a furnace. Computed amounts of  $Li_2CO_3$  and 10YSZ were mixed and carefully ground in an agate mortar. The mixture obtained was briquetted into 15.2 mm in diameter, 6–7 mm thick pellets at pressure 67 MPa. The samples were placed into corundum crucibles which were placed in a furnace and kilned for 24 h at 1200°C. Sintering was conducted in a single step without intermediate grinding of the materials.

The phase composition and ionic conductivity (ac current) of the samples obtained were investigated. X-ray phase analysis was performed with a DRON-3.5M ( $CuK_\alpha$  radiation) diffractometer. Standard data from the ASTM x-ray card catalog were used to identify the phases for the cubic  $Zr_{0.85}Y_{0.15}O_{1.93}$  (30-1468) and monoclinic  $ZrO_2$  (13-307) modifications.

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<sup>2</sup> Here and below — the molar content.

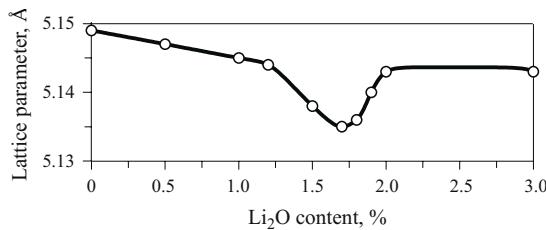


Fig. 1. Unit cell parameter of cubic 10YSZ versus the  $\text{Li}_2\text{O}$  content.

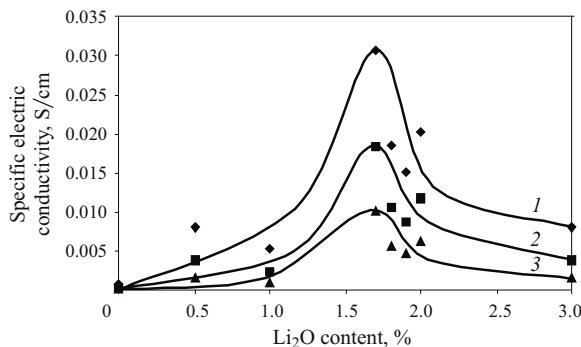


Fig. 2. Electric conductivity of 10YSZ samples versus  $\text{Li}_2\text{O}$  content at measurement temperatures  $500^\circ\text{C}$  (1),  $450^\circ\text{C}$  (2), and  $400^\circ\text{C}$  (3).

Silver electrodes were deposited on the ends of the experimental samples to measure the electric conductivity. The electrodes were formed by depositing a paste consisting of colloidal silver and rosin, after which the organic component was removed at  $650^\circ\text{C}$ . Then, the furnace was slowly cooled (over 8 h) together with the samples to room temperature. The ac electric conductivity was measured by the two-contact method in the temperature interval  $350 - 600^\circ\text{C}$ ; the working frequency for the measurements was 10 kHz. The measurements were performed with an E7-14 impedance meter, using a scheme where periods when the cell was allowed to cool alternating with periods when the temperature was held constant in order to establish constant values of the total resistance.

Analysis of the x-ray diffraction patterns showed that a single phase — cubic  $\text{ZrO}_2$  — is present in samples containing  $0 - 1.7\%$   $\text{Li}_2\text{O}$ . Above  $1.7\%$   $\text{Li}_2\text{O}$ , aside from the reflection lines of cubic  $\text{ZrO}_2$ , the x-ray diffraction patterns showed new peaks characteristic for the monoclinic phase of  $\text{ZrO}_2$ . The intensities of the reflection lines of monoclinic  $\text{ZrO}_2$  increase with increasing  $\text{Li}_2\text{O}$  concentration. No other phases were found in the experimental samples. Thus, samples with  $0 - 1.7\%$   $\text{Li}_2\text{O}$  are single-phase, and for  $1.8 - 3.0\%$   $\text{Li}_2\text{O}$  two phases of  $\text{ZrO}_2$  coexist: cubic and monoclinic.

The unit cell parameters of the cubic modification of  $\text{ZrO}_2$  were determined from the x-ray data for the experimental samples. The lattice parameter as a function of the  $\text{Li}_2\text{O}$  content is presented in Fig. 1. It is evident that the crystal lattice parameter tends to decrease when  $\text{Li}_2\text{O}$  is introduced into 10YSZ. The lowest value of the parameter is observed

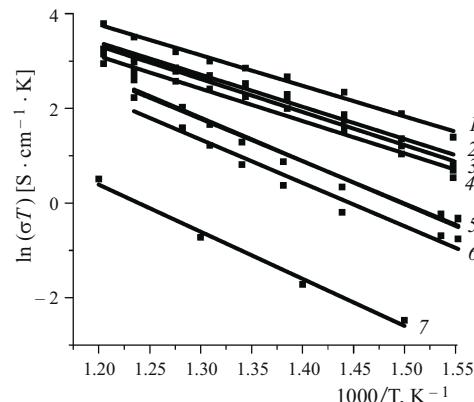


Fig. 3. Electric conductivity of 10YSZ samples, alloyed with  $\text{Li}_2\text{O}$ , in the coordinates  $\ln(\sigma T) = f(1000/T)$ . Content of  $\text{Li}_2\text{O}$ : 1) 1.7; 2) 2.0; 3) 1.8; 4) 1.9; 5) 0.5; 6) 1.0; 7) 0.

for  $1.7\%$   $\text{Li}_2\text{O}$ . The lattice parameter increases as the amount of  $\text{Li}_2\text{O}$  increases further.

The variation of a specific electric conductivity of the experimental samples as a function of the  $\text{Li}_2\text{O}$  content is shown in Fig. 2. The electric conductivity of 10YSZ increases when  $\text{Li}_2\text{O}$  is introduced, reaches a maximum value at  $1.7\%$   $\text{Li}_2\text{O}$ , and then decreases. The temperature dependences of the electric conductivity for samples with different  $\text{Li}_2\text{O}$  concentration are presented in Arrhenius coordinates in Fig. 3. It is evident from Figs. 2 and 3 that introducing lithium oxide into cubic 10YSZ substantially increases its conductivity.

Rectilinear lines describe the primary data on the conductivity in the Arrhenius coordinates quite well (see Fig. 3). This made it possible to calculate the effective values of the conduction activation energy  $E_a$  of the samples.

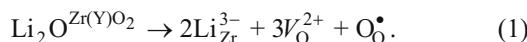
#### Electrical conduction activation energy of 10YSZ samples alloyed with $\text{Li}_2\text{O}$

$\text{Li}_2\text{O}$ content, %	$E_a$ , eV
0 . . . . .	$0.85 \pm 0.05$
0.5 . . . . .	$0.77 \pm 0.08$
1.0 . . . . .	$0.79 \pm 0.03$
1.7 . . . . .	$0.56 \pm 0.05$
1.8 . . . . .	$0.60 \pm 0.02$
1.9 . . . . .	$0.59 \pm 0.01$
2.0 . . . . .	$0.59 \pm 0.03$
3.0 . . . . .	$0.79 \pm 0.07$

The activation energy of conduction in 10YSZ samples with no  $\text{Li}_2\text{O}$  is  $0.85$  eV in the experimental temperature range. When  $\text{Li}_2\text{O}$  is added, the activation energy starts to decrease and passes through a minimum. The minimum value of  $E_a$ , equal to  $0.56$  eV, is observed at  $1.7\%$   $\text{Li}_2\text{O}$ .

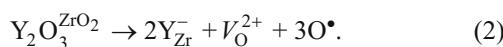
It is known that  $\text{Li}^+$  impurity ions in oxide crystals (for example,  $\text{ZnO}$ ,  $\text{BeO}$  [4, 5]) can replace extrinsic atoms at the regular lattice sites, forming substitution defects and they can

also occupy interstices. In the oxides of high valence crystals ( $\text{SiO}_2$ ,  $\text{GeO}_2$ ) the  $\text{Li}^+$  cations occupy interstices [6]. The ionic radius of a  $\text{Li}^+$  cation (0.68 Å) is less than that of the cation  $\text{Zr}^{4+}$  (0.82 Å) [7]. The decrease of the lattice parameter of cubic 10YSZ with the introduction of small amounts of  $\text{Li}_2\text{O}$  (see Fig. 1) gives a basis for supposing that a solid substitution solution forms with 0 – 1.7%  $\text{Li}_2\text{O}$ . The cations  $\text{Li}^{+2}$  occupy regular lattice sites, replacing zirconium  $\text{Li}^+ \rightarrow \text{Zr}^{4+}$  with  $\text{Li}_{\text{Zr}}^{3-}$  defects forming. The defects  $\text{Li}_{\text{Zr}}^{3-}$  possess a negative effective charge, which requires compensation. Positively charged oxygen vacancies  $V_{\text{O}}^{2+}$  can perform the compensation, just as in the case of the substitution  $\text{Y}^{3+} \rightarrow \text{Zr}^{4+}$ . The dissolution of  $\text{Li}_2\text{O}$  in 10YSZ can be represented by the quasichemical reaction



According to this reaction, three oxygen vacancies compensate two lithium ions occupying  $\text{Zr}^{4+}$  sites. Thus, if it is assumed that the ions occupy regular lattice sites, then the added  $\text{Li}_2\text{O}$  is the source of the additional oxygen vacancies in 10YSZ.

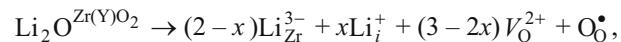
The appearance of additional oxygen vacancies could explain the large increase of the ionic conductivity in the experimental ceramic when  $\text{Li}_2\text{O}$  is introduced. It is known that the mechanism of ion transfer in stabilized cubic  $\text{ZrO}_2$  can be described by a model where oxygen ions hop along vacancies forming in an anionic sublattice when  $\text{Y}^{3+}$  replaces a zirconium cation  $\text{Zr}^{4+}$ . Thus, when a single  $\text{Y}_2\text{O}_3$  molecule dissolves in a zirconium dioxide lattice, two substitution defects  $\text{Y}_{\text{Zr}}^-$  and one oxygen vacancy appear:



In accordance with this equation, the initial zirconium dioxide stabilized by  $\text{Y}_2\text{O}_3$  (10YSZ), contains 10% to oxygen vacancies. When 1.7%  $\text{Li}_2\text{O}$  is added, taking account of the reaction (1), 5.1% additional oxygen vacancies should appear in the 10YSZ in lattice. The total number of anionic vacancies in 10YSZ containing 1.7%  $\text{Li}_2\text{O}$  should be approximately 15%. This is equivalent to alloying  $\text{ZrO}_2$  with 15%  $\text{Y}_2\text{O}_3$ . It is known that the cubic phase of  $\text{ZrO}_2$  is stabilized in a quite wide interval of molar content of  $\text{Y}_2\text{O}_3$  (8 – 40%). The concentration of oxygen vacancies grows proportionately as the amount of stabilizer increases, but the concentration dependence of the ionic conductivity is not linear but possesses a maximum at 15 – 16%  $\text{Y}_2\text{O}_3$ . The ionic conductivity with  $\text{Y}_2\text{O}_3$  content ranging from 10 to 15% increases by approximately a factor of 2 – 3 [8]. In the experimental samples of 10YSZ containing 1.7%  $\text{Li}_2\text{O}$  and oxygen vacancies equivalent to 15%  $\text{Y}_2\text{O}_3$  the ionic conductivity increases by more than an order of magnitude. This suggests that in this case other defects besides oxygen vacancies participate in charge transfer. The substantial decrease of the conduction

activation energy of 10YSZ samples alloyed with  $\text{Li}_2\text{O}$  also attests to this.

According to existing ideas, the conduction activation energy of stabilized cubic  $\text{ZrO}_2$  includes the formation energy of an active vacancy near a zirconium atom, which equals 0.5 – 0.6 eV, and the migration energy itself, equal to 0.7 – 0.8 eV [9, 10]. According to different experimental and theoretical data, the conduction activation energy of stabilized cubic  $\text{ZrO}_2$  depends on the temperature and the concentration of the stabilizer and lies in the range 0.85 – 1.33 eV [8 – 12]. The conduction activation energy obtained for 10YSZ samples alloyed with  $\text{Li}_2\text{O}$  is much lower than the values of  $E_a$  characteristic for anionic vacancy conductivity of cubic  $\text{ZrO}_2$ . This attests to the appearance of charge carriers with higher mobility than oxygen vacancies. In this case such charge carriers can be lithium ions occupying interstices —  $\text{Li}_i^+$ . In the materials for which lithium ion conduction is characteristic, the activation energy, as a rule, is less than  $E_a$  of oxygen-vacancy conduction and lies in the range 0.20 – 0.56 eV [13, 14]. Consequently, it must be assumed that lithium ions in 10YSZ can occupy not only regular lattice sites ( $\text{Li}_{\text{Zr}}^{3-}$ ) but also interstices ( $\text{Li}_i^+$ ):



where  $x$  is the fraction of lithium ions occupying interstices.

The partial self-compensation of oppositely charged defects ( $\text{Li}_{\text{Zr}}^{3-}$  and  $\text{Li}_i^+$ ) has the result that the real concentration of oxygen vacancies is lower than determined above. As the  $\text{Li}_i^+$  fraction increases in the material, the contribution of lithium-ion conduction increases, resulting in a lower effective conduction activation energy.

For  $\text{Li}_2\text{O}$  content above 1.7% the experimental ceramic becomes a two-phase material — the monoclinic phase  $\text{ZrO}_2$  appears. Apparently, the partial modification transformation of  $\text{ZrO}_2$  (cubic  $\rightarrow$  monoclinic) is due to lithium entering the 10YSZ lattice. This can be explained as follows. As the  $\text{Li}_2\text{O}$  content increases, the concentration of vacancy ions in 10YSZ decreases, since interstitial ions  $\text{Li}_i^+$  start to participate in the charge compensation of substitution defects  $\text{Y}_{\text{Zr}}^-$ . Yttrium oxide no longer acts as a stabilizer, as a result of which monoclinic  $\text{ZrO}_2$  is formed.

As a result of this work, polycrystalline samples of  $\text{ZrO}_2$ , stabilized with 10%  $\text{Y}_2\text{O}_3$ , with added  $\text{Li}_2\text{O}$  (0 – 3%) were synthesized. It was determined that for 0 – 1.7%  $\text{Li}_2\text{O}$  the samples retain the structure of the initial material, while at higher concentrations they are two-phase materials because of the appearance of a monoclinic  $\text{ZrO}_2$ .

It was assumed that the  $\text{Li}^+$  ions can occupy intrinsic lattice sites of  $\text{ZrO}_2$ , forming substitution defects  $\text{Li}_{\text{Zr}}^{3-}$ , and interstices, forming interstitial defects  $\text{Li}_i^+$ .

The introduction of lithium oxide increases the electric conductivity of stabilized  $\text{ZrO}_2$  in the temperature range 300 – 650°C by more than an order of magnitude as a result of the contribution of lithium-cation conduction.

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